(51) International Patent Classification ^{6} : **C08F 297/08, C10M 143/02, C09J 153/00, C08L 53/00 // (C10M 143/02, 143:00), C10N 20:02**	**A1**	(11) International Publication Number: **WO 95/27746** (43) International Publication Date: 19 October 1995 (19.10.95)

(21) International Application Number: PCT/US95/04250

(22) International Filing Date: 6 April 1995 (06.04.95)

(30) Priority Data:
08/223,912   6 April 1994 (06.04.94)   US

(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).

(72) Inventors: COZEWITH, Charles; 4810 Welford Drive, Bellaire, TX 77401 (US). VER STRATE, Gary, William; 162 Longwood Drive, Manalapan, NJ 07726 (US). WEST, Roger, Karl; 109 Montclair Avenue, Montclair, NJ 07042 (US). CAPONE, Gaetano, A.; 75 Beauvelt Avenue, Dumont, NJ (US).

(74) Agents: MILLER, Douglas, W. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).

(81) Designated States: AU, BR, CA, CN, JP, KR, MX, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: ETHYLENE α-OLEFIN BLOCK COPOLYMERS AND METHODS FOR PRODUCTION THEREOF

(57) Abstract

This invention relates to block polymers containing both crystalline and elastomeric blocks, the block copolymer having an A block and a B block. The A block is a polyethylene or an ethylene polymer optionally containing an alpha-olefin and optionally a non-conjugated diene, and is generally crystalline. The B block is an ethylene, α-olefin copolymer. Also disclosed is a process for manufacture of the block copolymers and methods for coupling the block copolymers. Coupled block copolymers are useful as thermoplastic elastomers exhibiting physical properties approaching those of crosslinked EP or EPDM elastomers, but showing thermal processability after coupling. The block copolymers of the present invention may also be used as a lubricant or fuel additive, as a plastics blend component, and as a component in hot melt adhesives.

APPLICATION FOR PATENT

5

Title: ETHYLENE α-OLEFIN BLOCK COPOLYMERS AND
              METHODS FOR PRODUCTION THEREOF

10

Technical Field

This invention relates to block polymers containing both crystalline and elastomeric blocks. The copolymers have blocks of polyethylene optionally containing an α-olefin and a non-conjugated diene and blocks containing ethylene and an α-olefin.
15   A novel process for producing the block copolymers is also provided.

BACKGROUND

Block copolymers are well known. They have been used commercially as
20   components in adhesives, as melt processable rubbers, in impact resistant thermoplastics, as compatibilizers, as "surfactants" for emulsifying polymer-polymer blends, and as viscosity index improvers in lubricating oils. A block copolymer is created when two or more polymer molecules of different chemical composition are covalently bonded in an end-to-end fashion. While a wide variety of block copolymer architectures are possible,
25   most block copolymers of interest involve the covalent bonding of hard plastic blocks, which are substantially crystalline or glassy, to elastomeric blocks forming thermoplastic elastomers. Other block copolymers, such as rubber-rubber (elastomer-elastomer), glass-glass, and glass-crystalline block copolymers are also possible and may have commercial importance. Two common types of block copolymer structures are the
30   diblock and tri-block forms. However, multi-block copolymers, in which more than three blocks are bonded together, are also desirable. The multi-block copolymers include either linear multi-block or multi-arm star block polymers.

Tri-block and multi-block copolymers containing "hard" and "soft" blocks have

- 2 -

the unique ability of behaving as thermoplastic elastomers, combining thermoplasticity with rubber-like behavior. The typical requirement for achieving thermoplastic elastomeric behavior is the ability to develop a two-phase physical network. Such a system is composed of a portion of hard block, having a glass transition temperature

5   (T_g) or melting temperature (T_m) above the service temperature of a fabricated end use product, and a portion of a soft block, having a T_g below the service temperature. The hard blocks associate to form domains that serve as physical crosslinks and reinforcement sites. The reinforcement sites and physical cross-links are thermally reversible, making it possible to process the polymer as a melt phase material at

10   temperatures above the T_g or T_m of the hard block. Among the advantages of having a physically cross-linked system that is thermally reversible is that while below the T_g or T_m of the hard block such polymers exhibit properties approaching those of fully-cured, i.e. chemically crosslinked elastomers, but unlike such cured elastomers, by heating these polymers above T_g or T_m of the hard block, the physical crosslinks are eliminated and

15   the material can be processed. The advantage of such systems will be well known to those of ordinary skill in the art.

A substantial amount of work has been done in an attempt to synthesize olefinic block copolymers. The ideal catalyst system would produce a "living polymer". Unlike

20   typical Ziegler-Natta polymerization processes, living polymerization processes involve only initiation and propagation steps and essentially lack chain terminating side reactions. This permits the synthesis of the predetermined and well-controlled structures desired in a block copolymer. A polymer created in a "living" system can have a narrow or extremely narrow distribution of molecular weight and be essentially monodisperse.

25   Living catalyst systems are characterized by an initiation rate which is on the order of or exceeds the propagation rate, and the absence of termination or transfer reactions. In addition, these catalyst systems are preferably characterized by the presence of a single type of active site. To produce a high yield of block copolymer product in a polymerization process the catalyst must exhibit living characteristics to a substantial

30   extent.

Anionic polymerization routes to ideal block copolymers have been studied. Butadiene-isoprene block copolymers have been synthesized using the sequential monomer addition technique. In sequential addition, a certain amount of one of the

35   monomers is contacted with the catalyst. Once a first such monomer has reacted to substantial extinction forming the first block, a certain amount of the second monomer or

- 3 -

monomer species is introduced and allowed to react to form the second block.   The process may be repeated using the same or other anionically polymerizable monomers. Ethylene and other α-olefins, such as propylene and butene, are not directly block polymerizable by anionic techniques.

5

   U.S. patent 4,804,794 to Ver Strate, et al., discloses segmented copolymers of ethylene and at least one other alpha-olefin. The copolymers have a narrow MWD (Mw/Mn) less than 2. The copolymers have one segment that is crystallizable and at least one low crystallinity segment.   A vanadium catalyst is utilized with an organoaluminum

10   cocatalyst. The polymerization is carried out in a mix-free reactor.

   WO 9112-285-A to Turner, et al., discloses a process for production of block copolymers of ethylene with an alpha-olefin and the polymer produced by the process. The process includes sequentially contacting ethylene with an alpha-olefin in the

15   presence of an ionic catalyst to produce a block copolymer. The ionic catalyst comprises the reaction product of a first component which is a bis (cyclopentadienyl) derivative of a metal of Group IV-B of the Periodic Table of the Elements which metal is capable of forming a cation formally having a coordination number of 3 and a valence of -4; and at least one second component comprising a cation capable of donating a proton and a

20   compatible non coordinating anion.

   While many patents and publications claim the Ziegler-Natta catalyzed synthesis of block copolymers from ethylene and propylene, there is little evidence that these products were obtained in high purity.   In Boor, J. Ziegler-Natta Catalysts and

25   Polymerization, Academic Press, 1979, Boor states that the known kinetic features of heterogeneous Ziegler-Natta catalysts suggest that it is unlikely that block polymers were synthesized in a substantial yield, as compared to the total polymer formed.   This publication is incorporated herein by reference for purposes of U.S. patent practice.

30   In this context, several difficulties arise in the use of known coordination catalysts for the block copolymerization of α-olefins. Among those are the fact that conventional catalysts are typically multi-sited, and a significant fraction of the active sites are unstable. This leads to non-uniform chain initiation and termination which, in turn, lowers the theoretical block copolymer yield. In addition, chain transfer rates

35   during polymerization with known coordination catalysts are high. This is especially true with metallocene catalyst systems where thousands of chains may be produced per active

- 4 -

site.

SUMMARY

The present invention is directed to procedures to make the use of certain coordination catalysts possible for production of alpha-olefin block copolymers of the crystalline-elastomeric type in high purity. These block copolymers and methods of their manufacture by a Ziegler-Natta type catalyst are objects of our invention. We will demonstrate the existence of high yields of true block copolymers. Evidence of the existence of such high yield of true block copolymer, as stated above, has been substantially absent prior to the present invention.

The present invention comprises a novel block polymer having an A block and a B block, and if a diene is present in the A block, a nodular polymer formed by coupling two or more block polymers. The A block is an ethylene polymer optionally containing an alpha-olefin and /or a non-conjugated diene. The diene, if present in the A block, is present in an amount up to 10 mole percent based on the total moles of the monomers of the block copolymer. The B block has a first polymer segment that is an ethylene and an alpha-olefin copolymer segment, the first polymer segment is contiguous to a junction of the A block and the B block. The B block may have a tip segment, the tip segment is furthest from the A B junction, and the tip segment is a polymer of ethylene and an alpha-olefin. The tip segment of the B block may comprise an ethylene, alpha-olefin copolymer with an average ethylene content of at least 60 mole percent based on the total tip segment, the tip segment melts in the range of from 35° C to 130° C as measured by DSC.

The present invention also comprises a process for producing these block copolymers, which has the steps of:

(a) Forming a catalyst species by premixing a vanadium compound and an organoaluminum compound. The pre-mixing step is carried out for a sufficient period of time to provide an adequate amount of active catalyst species;

(b) Feeding the reaction product of step (a) to a mix free reactor concurrently with a monomer stream made up of ethylene, optionally an alpha-olefin and optionally a non-conjugated diene;

- 5 -

(c) Feeding at least a second monomer blend made up of ethylene, and an alpha-olefin;

If a diene is present, the block copolymer may be coupled using the residual olefinic functionality of the diene to produce nodular polymers. Coupling can take place either in the reactor, or post reactor.

The coupled polymer will generally be useful in, among other applications, lubricating oils, as viscosity improvers or dispersants. A coupling agent may be used to couple two or more block copolymers.

These block copolymers find use as thermoplastic elastomers (TPE), plastics blending components, in fuel lubricating and heating oils, as a bitumen modifier, in roof sheeting compounds, and in hot melt adhesives.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following description, appended claims and accompanying drawings where:

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a Differential Scanning Calorimeter (DSC) thermogram for polymer 2A described in Example 2.

Figure 2 is a DSC thermogram for polymer 2B described in Example 2.

Figure 3 is a DSC thermogram of a pure polyethylene A block.

Figure 4 is a schematic representation of a process for producing polymer in accordance with our invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to procedures to make and use certain alpha-olefin block copolymers of the crystalline-elastomeric type in high purity using certain

- 6 -

coordination catalysts. These block copolymers and methods of their manufacture by a
Ziegler-Natta type catalyst are among the objects of our invention.

The present invention comprises a novel block copolymer having an A block and
a B block and when a diene is present in the A block, a nodular polymer formed by
coupling two or more block copolymers. The nodular polymer may optionally contain a
coupling agent Y;

(1)   "A" denotes a block comprising polyethylene, and optionally an α-olefin
        comonomer not exceeding 5 mole percent based on the total moles of monomers
        in the A block, and further optionally containing up to 10 mole percent of a non-
        conjugated diene. The diene is present at this mole percent based on the total A
        B block copolymer.

The A block is present in the block copolymer preferably in the range of from 5
to 90 weight percent based on the total weight of the block copolymer. More preferably
in the range of from 10 to 60 weight percent, most preferably in the range of from 20
to 50 weight percent.

(2)   "B" denotes a block comprising ethylene and an α-olefin copolymer. The B
        block comprises one or more segments. If there is one segment in the B block, it
        will be an ethylene, α-olefin segment. If there are two or more segments in the B
        block, the first segment immediately following the junction of the A and B blocks
        will be an ethylene α-olefin copolymer segment. The tip or end segment will be
        located in the portion of the B block furthest from the A B junction. If there are
        two segments, the second or tip segment will be an ethylene, α-olefin copolymer
        with an average ethylene content of at least 60 mole percent based on the total
        moles of the monomers of the tip segment, and which melts in the range of 35 to
        130°C, as measured by DSC.

Optionally the B block has an intramolecular composition distribution such that
at least two portions of the B block, each portion comprising at least 5 weight percent of
the B block, differ in composition by at least 5 weight percent ethylene. The B block is
present in the block copolymer in the range of from 10 to 95 weight percent based on
the total weight of the block copolymer.

The tip of the B block can comprise up to 50 weight percent of the B block, preferably in the range of from 3 to 20 weight percent, more preferably in the range of from 5 to 15 weight percent, all weight percents of the tip based on the total weight of the B block. The tip segment, when present, is typically the segment furthest from the A B junction.

Y is a coupling agent which has reacted with the residual olefinic functionality in the block polymers and has coupled two or more block polymer molecules.

A is a crystalline block and B has elastomeric segments. B may optionally contain a low level of crystallinity.

COPOLYMER BLOCKS

BLOCK A

Block A comprises polyethylene which optionally may contain up to 10 mole percent of a non-conjugated diene (based on the total moles of the monomers of the A B copolymer). The A block may optionally contain an α-olefin comonomer at a level not exceeding 5 mole percent based on the total moles of the monomers of the A block. If block A contains a non-conjugated diene it will be present in the A block preferably in the range of from 0.01 to 5 mole percent, more preferably in the range of from 0.03 to 2 mole percent, most preferably in the range of from 0.05 to 1 mole percent based on the total moles of the monomers of the A B block copolymer. Block A comprises 5 to 90 weight percent of the entire polymer, preferably 10 to 60 weight percent , most preferably 20 to 50 weight percent of the entire polymer. The A block has a T_m of at least 110° C, preferably at least 105° C, more preferable at least 120° C.

BLOCK B

Block B is an elastomer that comprises an ethylene and an α-olefin copolymer. Block B optionally has an intramolecular-compositional distribution such that at least two portions of the B block, each of said portions comprising at least 5 weight percent of said B block, differ in composition by at least 5 weight percent ethylene. Intramolecular-compositional distribution is the compositional variation, in terms of ethylene, along the polymer chain or block. It is expressed as the minimum difference in

- 8 -

average ethylene composition in weight percent of ethylene that exists between two portions of a single block, each portion comprising at least 5 weight percent of the block. Intramolecular-compositional distribution is determined using the procedures disclosed in U.S. Patent No. 4,959,436, the teachings of which are hereby incorporated by reference for purposes of U.S. patent practice.

The B block comprises 95 to 10 weight percent of the total weight of the block copolymer, preferably 90 to 40 weight percent; more preferably 80 to 50 weight percent.

The B block comprises one or more segments. If there are two or more segments in the B block, the tip or end segment furthest from the junction of the A block and the B block will comprise an ethylene, α-olefin copolymer with an average ethylene content of at least 60 mole percent based on the total moles of the monomers of the tip segment. The tip segment melts in the range of from 35° C to 130° C as measured by DSC

The tip of the B block can comprise up to 50 weight percent of the B block, preferably in the range of from 3 to 20 weight percent, more preferably in the range of from 5 to 15 weight percent, all weight percents of the tip based on the total weight of the B block. The tip segment, when present, is typically the segment furthest from the A B junction.

The B block can comprise an average ethylene content in the range of from 20 to 90 mole percent, preferably in the range of from 30 to 85 mole percent, and most preferably in the range of from 50 to 80 mole percent based on the total moles of the monomers of the B block.

The block copolymers of the invention are further characterized in that they have a number average molecular weight of between 750 and 20,000,000 and have a molecular weight distribution characterized by a M_w/M_n ratio of less than 2.5. The block copolymers have an n-hexane soluble portion, at 22 °C not exceeding 50 weight percent, preferably not exceeding 40 weight percent, and more preferably not exceeding 30 weight percent, based on the total weight of the block copolymer. The products of the present invention are further characterized by a relatively small amount of polymer chains in the final product that contain only an A block or only a B block. The presence of such materials could detract from overall product properties. A typical characteristic

of the preferred product of this invention is that the block copolymer contains at least 50 % (weight) of the desired A B structure as polymerized. Product purification is not necessary to obtain good properties.

5   Monomers

Alpha-olefins particularly useful in the practice of this invention are those having from 3 to 8 carbon atoms, e.g. propylene, butene-1, pentene-1, etc. Alpha-olefins of 3 to 6 carbon atoms are preferred due to economic considerations. The most preferred α-olefin is propylene.

Typical non-limiting examples of non-conjugated dienes useful in the practice of this invention are:

15   (a)   straight chain acyclic dienes such as: 1,4-hexadiene; 1,6-octadiene;

(b)   branched chain acyclic dienes such as: 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-dioctadiene; and the mixed isomers of dihydromyrcene and dihydro-ocinene;

20

(c)   single ring dienes such as: 1,4-cyclohexadiene; 1,5-cyclooctadiene; and 1,5-cyclododecadiene;

(d)   multi-ring fixed and fused ring dienes such as: tetrahydroindene; methyltetra-
25   hydroindene; dicyclopentadiene; bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-ethylidene-2-norbornene (ENB), 5-propenyl-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, vinyl norbornene, and norbornadiene.

30

Of the non-conjugated dienes useful in the practice of the invention, dienes containing at least one of the double bonds in a strained ring are preferred. The most preferred dienes are 5-ethylidene-2-norbornene and vinyl-norbornene. Conjugated dienes are also contemplated.

- 10 -

Polymerization

        The novel polymers of our invention are prepared by polymerization in a mix-free
5   reactor similar to that taught in U.S. Patent No. 4,959,436, the teachings of which were
previously incorporated by reference for the purposes of U.S. patent practice.

        Previously, those of skill in the art thought that a solution polymerization process
such as that taught in U.S. Patent No. 4,959,436 would not be suitable for producing
10   block copolymers such as the ones described above in which one of the blocks,
polyethylene, is insoluble in the solvent. The insolubility could lead to reactor fouling and
mass transport problems. In turn, these problems could prevent the formation of the
desired well-defined polymer structure and significantly reduce catalyst efficiency.

15   Surprisingly, we have found that the block polymers of our invention can be
made in a mix-free reactor when the initial monomer feed consists essentially of ethylene,
and optionally such that up to 5 mole percent of the A block is alpha-olefin and
optionally a diene sufficient to incorporate up to 10 mole percent of a non-conjugated
diene (based on the total of the monomers of the block copolymer). This, the A block, is
20   polymerized first. During this part of the reaction, the polyethylene (A) block may be
only partially soluble in the reaction diluent and the insoluble polymer block forms a
suspension in the diluent.

        Once the polymerization of the A block is substantially complete, one or more
25   additional monomer feeds are introduced into the reactor containing ethylene, and an α-
olefin. The reaction of the comonomer mixtures forms the B block of the block polymer
or the first segment of the B block if there is more than one segment. The B block is
polymerized onto the polyethylene or A block formed earlier. When this second part of
the polymerization occurs, there is a noticeable change in the appearance of the reaction
30   medium. As the chains become solubilized through the addition of the B block, the
turbidity of the medium decreases appreciably and the quantity of polymer particles in
the diluent is markedly reduced. When a tubular reactor is employed, several monomer
feeds along the reactor length may be used to control the composition and amount of the
B block and form the segments of the B block. The final feeds to the reactor may
35   contain a higher ethylene/α-olefin ratio to form a semi-crystalline segment at the tip of
the B block., giving the B block a melting point in the range of from 35 to 130° C.

- 11 -

Coupling the Polymers

Block polymers of our invention may incorporate a diene. The residual olefinic functionality in diene containing block polymers can be reacted with coupling agents to produce novel nodular polymers.

Suitable coupling reagents and coupling techniques are described in U.S. Patent 4,882,406 the teachings of which have previously been incorporated by reference for purposes of U.S. patent practice. Coupling can take place either within the polymerization reactor or in a post-polymerization reaction. With the diene in the A block, the polyethylene segment containing the diene is in a central polyethylene nodule with EP block extending outwards.

There are various coupling agents that are capable of reacting with the residual unsaturation in the polymer chains to cause coupling of two or more block polymer molecules.

Coupling may be carried out with cationic catalysts such as Lewis acids. Suitable Lewis acids may be selected from the group consisting of: AlX_3, BX_3, SnX_4, SbX_5, AlR_yX_{3-y} where y is 0 to 1.5 and R is a hydrocarbon radical, BX_4, TiX_4 and mixtures thereof, where X is selected from the group consisting of chlorine, bromine, and iodine. Chlorine is preferred. For Lewis acids that do not interfere with the functioning of the catalyst system used to carry out the polymerization, the Lewis acid can be added directly to the reactor so that chain coupling occurs at the same time as the polymerization. Alternately the coupling agent can be added following the polymerization.

According to yet another embodiment the coupling agent may be a free radical catalyst. The free radical catalyst may be a peroxide selected from the group consisting of: dicumyl peroxide, di-tertiarybutylperoxide, t-butylperbenzoate, 1,1-di(t-butylperoxy)-3,3,5-trimethyl cyclohexane, and mixtures thereof. Other free radical catalysts include azo-bisisobutylnitrile, azodicarboxylate, and mixtures thereof. Peroxides can couple non-diene containing portions of the chain and produce a cross-linked network. Care must be taken when they are used as coupling agents.

- 12 -

In yet another embodiment the coupling agent may be selected from the group consisting of sulfur dichloride, disulfenyl halides, borane, dithoalkanes, other sulfur and accelerated sulfur curatives and mixtures thereof, such as mercaptobenzothiozole, tetramethylthiuram disulfide, and butyl zymate. It is apparent that any of the conventional vulcanization systems useful for EPDM may be employed.

Resins and other reagents may also be employed for coupling. For example alkyl phenol formaldehyde mixtures will couple olefins in certain cases with catalysts such as $ZnCl_2$, N-bromosuccinimide or diphenylbromomethane.

Also contemplated as a coupling mechanism is the use of irradiation or electron beams.

For certain non-conjugated dienes, such as norbornadiene, vinyl norbornene, dicyclopentadiene and tetrahydroindene, both double bonds are polymerizable to a greater or lesser extent by the polymerization catalysts of this invention. With dienes of this type chains can become chemically coupled to each other during polymerization by reaction of the remaining double bond in an enchained diene monomer with a growing chain. This process will lead to coupling of chains in the reactor even in the absence of a coupling agent Y.

The efficiency of olefin utilization will determine what level of coupling agent to use in relation to the amount of diene in the block copolymer. The purpose is to couple the diblocks to an extent which yields good mechanical properties but does not raise viscosity or produce gel to the extent that the coupled product is not processable.

The Reaction Solvent

Processes in accordance with the present invention produce copolymers by polymerization of a reaction mixture comprised of catalyst, ethylene and at least one additional α-olefin monomer and optionally diene. Polymerization in the presence of a diluent which has the capability to dissolve a major portion of the final product is preferred. Suitable solvents are described in U.S. patent number 4,882,406 the teachings of which are incorporated by reference for purposes of U.S. patent practice.

- 13 -

Polymerization Reactor

These processes are carried out in a mix-free reactor system, which is one in which substantially no mixing occurs between portions of the reaction mixture that
5   contain polymer chains initiated at different times. Suitable reactors are disclosed in U.S. patents 4,959,436 and 4,882,406 both of which have been incorporated by reference for the purposes of U.S. patent practice. Additional reaction considerations are also disclosed in these references.

10   To obtain the desired A B block polymer, it is necessary to add additional reactants (e.g., at least one of the monomers ethylene, α-olefin or diene) either at some point or points along the length of a tubular reactor, or during the course of polymerization in a batch reactor, or at various points in a train of continuous flow stirred reactors. However, it is also preferred to add essentially all of the catalyst at the
15   inlet of a continuous flow reactor or at the onset of batch reactor operation to meet the requirement that essentially all polymer chains are initiated simultaneously. To make diene containing block polymers, diene is fed at the reactor inlet to incorporate diene into an A block. Multiple feeds of ethylene and propylene can be used to control the amount and composition of the segments in the B block.
20

Since the tubular reactor is the preferred reactor system for carrying out processes in accordance with the preferred embodiment, the illustrative descriptions and examples that follow are drawn to that system, but will apply to other reactor systems as will readily occur to those of ordinary skill in the art having the benefit of the present
25   disclosure. However, as would readily occur to those of ordinary skill in the art having the benefit of the present disclosure, more than one reactor could be used, either in parallel, or in series with multiple monomer feeds to vary intramolecular composition.

The Catalyst

30

The composition of the catalyst used to produce ethylene, α-olefin copolymers has a prof embodiment should be such as to yield essentially one active catalyst species in the reaction mixture. More specifically, it should yield one primary active catalyst species which provides for substantially all of the polymerization reaction. Additional active
35   catalyst species could be present, provided that they do not produce a significant amount of polymer which detracts from the performance of the polymer produced. Such

- 14 -

additional active catalyst species may provide as much as 35% by weight of the total copolymer. Preferably, they should account for 10% by weight or less of by the copolymer. Thus, the essentially one active species should provide for at least 65% by weight of the total copolymer produced, preferably for at least 90% by weight thereof.

5   The extent to which a catalyst species contributes to the polymerization can be readily determined using the below-described techniques for characterizing catalyst according to the number of active catalyst species. Techniques for characterizing catalyst according to the number of active catalyst species are within the skill of the art. These techniques are shown in Cozewith, C. and Ver Strate, G., "Ethylene-Propylene Copolymers.

10   Reactivity Ratios, Evaluation and Significance", Macromolecules, 4, 482 (1971), which is incorporated herein by reference for purposes of U.S patent practice.

The preferred catalyst system in practicing processes in accordance with these embodiments comprises a hydrocarbon-soluble vanadium compound in which the

15   vanadium valence is 3 to 5 and an organo-aluminum compound, with the provision that the catalyst system yields essentially one active catalyst as described above. At least one of the vanadium compound/organo-aluminum pair selected must also contain a valence-bonded halogen. Vanadium compounds useful in practicing processes in accordance with the present invention could be:

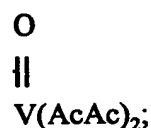$$\overset{\overset{\textstyle O}{\textstyle \|}}{VCl_x(OR)_{3-x};} \qquad (1)$$

$$VCl_x(COOR)_{3-x}; \qquad (2)$$

where x = 0 to 3 and R = a hydrocarbon radical;

$$VCl_4;$$

$$\overset{\overset{\textstyle O}{\textstyle \|}}{V(AcAc)_2;}$$

$$V(AcAc)_3;$$

$$\overset{\overset{\textstyle O}{\textstyle \|}}{VCl_x(AcAc)_{3-x};} \qquad (3)$$

where AcAc = acetyl acetonate; and where x = 1 or 2; and

$$VCl_3 \cdot nB;$$
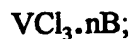
where n = 2 to 3 and B = Lewis base capable of making hydrocarbon-soluble complexes with VCl_3, such as tetrahydrofuran, 2-methyl-tetrahydrofuran and dimethyl pyridine. In Formulas (1) and (2) above, R preferably represents a C_1 to C_{10} aliphatic, alicyclic or aromatic hydrocarbon radical such as ethyl (Et), phenyl, isopropyl, butyl, propyl, n-butyl, i-butyl, t-butyl, hexyl, cyclohexyl, octyl, naphthyl, etc. Non-limiting illustrative examples of formulas (1) and (2) compounds are vanadyl trihalides, alkoxy halides and alkoxides such as $VOCl_3$, $VOCl_2(OBu)$ where Bu = butyl, $VO(OC_2H_5)_3$, and vanadium dichloro hexanoate. The most preferred vanadium compounds are VCl_4, $VOCl_3$, and $VOCl_2(OR)$.

As already noted, the co-catalyst is preferably an organoaluminum compound. In

- 16 -

terms of chemical formulas, these compounds could be as follows:

AlR_3	$Al(OR')R_2$
AlR_2X	$R_2Al-O-AlR_2$
$AlR'RX$	
$Al_2R_3X_3$	
$AlRX_2$	methyl alumoxane

where R and R' represent hydrocarbon radicals, the same or different, as described above with respect to the vanadium compound formula and X is a halogen selected from the group consisting of bromine, iodine, and chlorine. Chlorine is preferred. The most preferred organoaluminum compound for use with a vanadium catalyst is an aluminum alkyl sesquichloride such as $Al_2Et_3Cl_3$ or $Al_2(iBu)_3Cl_3$. The catalyst and its effects on the polymerization are disclosed in U.S. patent 4,882,406, previously incorporated by reference for purposes of U.S patent practice.

With reference again to processes for making copolymer in accordance with our invention, certain combinations of vanadium and aluminum compounds that can comprise the catalyst system can cause branching and gellation during the polymerization for polymers containing high levels of diene. To prevent this from happening, Lewis bases such as ammonia, tetrahydrofuran, pyridine, tributylamine, tetrahydrothiophene, tetraalkoxysilane, etc., can be added to the polymerization system using techniques well known to those skilled in the art.

Chain transfer reactions during tubular reactor polymerization in accordance with our invention broadens polymer molecular weight distribution and causes the formation of undesirable blocks such as A-only polymer or B-only polymer rather than the desired A B block copolymers of the present invention. It is desireable to operate at low temperature and in the absence of Hydrogen to avoid transfer reactions. U.S. patent 4,882,406 discloses chain transfer reactions. This U.S. patent has previously been incorporated by reference.

Molecular weight distribution and percent of block polymer in the final product are also affected by catalyst deactivation during the course of the polymerization which leads to termination of growing chains. Early chain termination will reduce the yield of the desired block copolymers. Deactivation can be reduced by using the shortest residence time and lowest temperature in the reactor that will produce the desired

monomer conversions.

Gel Permeation Chromatography (GPC) and several analytical techniques are used to characterize the polymer and its performance in various applications. These techniques have been described in several publications notably U.S. Patent No. 4,989,436 which has been previously incorporated for purposes of U.S. patent practice. Molecular weight and composition measurements are described in G. Ver Strate, C. Cozewith, S. Ju, Macromolecules, 21, 3360 (1988). The variety of other techniques used are soundly based in polymer structure characterization as described in "Structure Characterization" The Science and Technology of Elastomers, F. Eirich, editor, Academic Press 1978 Chapter 3 by G. Ver Strate. Differential scanning calorimetry (DSC) is used to characterize the block polymers described herein. The standard protocol for these analysis is to load the calorimeter at 20° C with a specimen free of molding strains, to cool the sample to -75° C, scan to 180° C at 10° C/min., cool to -75° C, and re-run the scan. T_g, T_m and heat of fusion are evaluated. In some cases, low melting crystallinity will not be seen on the second scan as it may take many hours to develop even at low temperatures.

Catalyst Preparation

Polymerizations in accordance with the preferred embodiments should be conducted in such a manner and under conditions sufficient to initiate propagation of essentially all copolymer chains simultaneously. This can be accomplished by utilizing the process steps and conditions described in U.S. patent 4,959,436, previously incorporated by reference for purposes of U.S. patent practice.

Reaction Temperature

The temperature of the reaction mixture should also be kept within certain limits. The temperature at the reactor inlet should be high enough to provide complete, rapid chain initiation at the start of the polymerization reaction. The length of time the reaction mixture spends at high temperature must be short enough to minimize the amount of undesirable chain transfer and catalyst deactivation reactions. Control of the reaction temperature in light of the fact that the reaction is exothermic, is disclosed in U.S. patent 4,959,436 which has been incorporated by reference for purposes of U.S. patent practice.

- 18 -

Residence Time

Residence time of the reaction mixture in the mix-free reactor can vary over a wide range. The minimum could be as low as 0.5 seconds. A preferred minimum is 2 seconds. The maximum could be as high as 3600 seconds. A preferred maximum is 900 seconds. The most preferred maximum is 300 seconds.

Process Flow

When a tubular reactor is used the rate of flow of the reaction mixture through the reactor should be high enough to provide good mixing of the reactants in the radial direction and minimize mixing in the axial direction. Good radial mixing promotes homogeneous temperature and polymerization rate at all points in a reactor cross section. Radial temperature gradients may tend to broaden the molecular weight distribution of the copolymer since the polymerization rate is faster in the high temperature regions. Those of ordinary skill in the art will recognize that achievement of these objectives is difficult in the case of highly viscous solutions. This problem can be overcome to some extent through the use of radial mixing devices such as static mixers (e.g., those produced by the Kenics Corporation).

For purposes of illustration, we assume that a block copolymer of polyethylene and of ethylene and propylene (EP) copolymer is to be produced using as catalyst components vanadium tetrachloride and ethyl aluminum sesquichloride. The polymerization is adiabatic, using hexane diluent for both the catalyst system and the reaction mixture.

In a preferred embodiment, with reference to the process flow diagram in Figure 4, the premixing device 1 comprises a temperature control bath 2, a fluid flow conduit 3 and mixing device 4 (e.g., a mixing tee). To mixing device 4, are fed hexane solvent, vanadium tetrachloride and ethyl aluminum sesquichloride through feed conduits 5, 6 and 7, respectively. Upon being mixed in mixing device 4, the resulting catalyst mixture is caused to flow within conduit 3, optionally in the form of a coiled tube, for a time long enough to produce the active catalyst at the temperature set by the temperature bath. The temperature of the bath is set to give the desired temperature in conduit 3, at the outlet of the bath. Upon leaving the premixing device, the catalyst solution flows

- 19 -

through conduit 8 into mixing zone 9, where it is intimately mixed with a stream containing hexane diluent and the monomer to be incorporated into the A block, in this case ethylene, and which is fed through conduit 10. Any suitable mixing device can be used such as mechanical mixer, orifice mixer or mixing tee. For economic reasons, the
5   mixing tee is preferred. The residence time of the reaction mixture in mixing zone 9, is kept short enough to prevent significant polymer formation therein before being fed through conduit 11 to tubular reactor 12. Alternatively, streams 8 and 10 can be fed directly to the inlet of reactor 12, if the flow rates are high enough to accomplish the desired level of intimate mixing. Stream 10, the hexane with dissolved monomers, may
10 be cooled upstream of mixing zone 9 to provide the desired feed temperature at the reactor inlet.

Tubular reactor 12 is shown with intermediate feed points 13, 14, and 14a where additional monomers (e.g., ethylene and propylene) and/or hexane can be fed to the
15 reactor. The additional feeds are used to control the composition of the block copolymer. The number of side feeds required and the spacing along the reactor length depends on final polymer structure desired. While the reactor can be operated adiabatically, external cooling means such as a cooling jacket surrounding at least a portion of the reactor system 12, can be provided to maintain reaction mixture
20 temperature within desired limits.

Having thus described the above illustrative reactor system, it will readily occur to those of ordinary skill in the art that many variations can be made within the scope of the present invention. For example, the placement and number of multiple feed sites, the
25 choice of temperature profile during polymerization and the concentrations of reactants, can be varied to suit the end-use application.

Functionalization of the Block Copolymers

30 The polymers produced in accordance with the present invention can be functionalized, i.e., chemically modified, to have at least one functional group present within its structure, which functional group is capable of: (1) undergoing further chemical reaction (e.g. derivatization) with other material/or (2) imparting desirable properties not otherwise possessed by the polymer alone, absent chemical modification.
35 The functional group can be incorporated into the backbone of the polymer or can be attached as a pendant group from the polymer backbone. The functional group typically

- 20 -

will be polar and contain hetero atoms such as P, O, S, N, halogen and/or boron. It can be attached to the saturated hydrocarbon part of the polymer via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer by oxidation or cleavage of a
5   small portion of the diene containing portion of the polymer (e.g., as in ozonolysis). Useful functionalization reactions include: maleation, halogenation, "ene" reactions, reactions with a phenol group, reaction at the point of unsaturation with carbon monoxide, reaction by free radical addition or abstraction and reaction by epoxidation or chloroamination.
10

As indicated, a functionalized polymer is one which is chemically modified primarily to enhance its ability to participate in a wider variety of chemical reactions than would otherwise be possible with the unfunctionalized polymer. In contrast, a derivatized polymer is one which has been chemically modified to perform one or more functions in
15   a significantly improved way relative to the unfunctionalized polymer and/or the functionalized polymer. Representative of such functions are dispersancy and/or viscosity modification in lubricating oil compositions. The derivatized polymers can include the reaction product of the above recited functionalized polymer with a nucleophilic reactant, which includes amines, alcohols, amino-alcohols and mixtures thereof, to form
20   oil soluble salts, amides, imides, oxazolines, reactive metal compounds and esters of mono- and dicarboxylic acids, and anhydrides. Suitable properties sought to be imparted to the derivatized polymer include especially dispersancy, but also multifunctional viscosity modification, antioxidancy, friction modification, antiwear, antirust, anti-seal swell, and the like.
25

Ash-producing detergents can be made using the functionalized polymers of the present invention as exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with alkyl phenols, alkyl sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such
30   as those prepared from the functionalized olefin polymer of the present invention with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, and sulfur, white phosphorus and a sulfur halide, or phosphorothiotic chloride. Preferred ash-producing detergents which can be derived from the functionalized polymers of the present invention include the metal salts of alkyl
35   sulfonic acids, alkyl phenols, sulfurized alkyl salicylates, alkyl naphthenates and other oil soluble mono- and dicarboxylic acids.

The derivatized polymer compositions of the present invention, can be used as ashless dispersants in lubricant and fuel compositions. Various types of ashless dispersants can be made by derivatizing the polymer of the present invention and are suitable for use in the lubricant compositions. The following are illustrative:

1.   Reaction products of functionalized polymer of the present invention derivatized with nucleophilic reagents such as amine compounds, e.g. nitrogen containing compounds, organic hydroxy compounds such as phenols and alcohols.

2.   Reaction products of the polymer of the present invention functionalized with an aromatic hydroxy group and derivatized with aldehydes (especially formaldehyde) and amines especially polyalkylene polyamines, through the Mannich reaction, which may be characterized as "Mannich dispersants".

3.   Reaction products of the polymer of the present invention which have been functionalized by reaction with halogen and then derivatized by reaction with amines (e.g. direct amination), preferably polyalkylene polyamines.

The functionalized polymers, particularly acid functionalized polymers, of the present invention can be reacted with alcohols, e.g., to form esters. Procedures are well known for reacting high molecular weight carboxylic acids with alcohols to produce acidic esters and neutral esters. These same techniques are applicable to preparing esters from the functionalized polymer of this invention and the alcohols described above. The hydroxy aromatic functionalized polymer aldehyde/amino condensates useful as ashless dispersants in the compositions of this invention include those generally referred to as Mannich condensates. A useful group of Mannich Base ashless dispersants are those formed by condensing phenol functionalized polymer with formaldehyde and polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxpropylene amines, e.g., polyoxyproylene diamine and combinations thereof.

A useful class of nitrogen containing condensation products for use in the present invention are those made by a "2-step process" as disclosed in U.S. Patent No. 4,273,891. Condensates made from sulfur-containing condensates are described in U.S. Patent Nos. 3,368,972; 3,649,229; 3,600,372; 3,649,659; and 3,741,896 These patents

also disclose sulfur-containing Mannich condensates. Useful reactive metals or reactive metal compounds are those which will form metal salts or metal-containing complexes with the functionalized polymer.

5   The polymer of the present invention may be used as a component of a synthetic base oil. The functionalized polymer, in addition to acting as intermediates for dispersant manufacture, can be used as a molding release agent, molding agent, metal working lubricant, thickeners and the like. The additives of the present invention are primarily useful in lubrication oil compositions which employ a base oil in which the additives are
10   dissolved or dispersed therein. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubrication oil composition of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like.
15

        Lubricating oil formulations containing the additives of the present invention conventionally contain other types of additives that contribute other characteristics that are required in the formulation. Typical of such other additives are detergent/inhibitors, viscosity modifiers, wear inhibitors, oxidation inhibitors, corrosion inhibitors, friction
20   modifiers, foam inhibitors, rust inhibitors, demulsifiers, lube oil flow improvers, and seal swell control agents, etc.

                              APPLICATIONS

25   Use in Lubricating Oils

        The novel block copolymers of the invention may be used as viscosity modifiers or with suitable functionalization and/or derivatization, as multifunctional viscosity modifiers, and as dispersants, for lubricating oils. This is especially true for block
30   polymers where there is a diene in the A block, and the polymers are in turn coupled to form a nodular polymer. From studies of hydrogenated block polymers of polyisoprene and polybutadiene, those of ordinary skill in the art are aware that such structures lead to good viscosity-temperature behavior (Ver Strate, G., Struglinski, M., "Polymers as Rheology Modifiers," Schulz, D. & Glass, J., ed. ACS Symp. 462, p. 257, 1991). Use
35   of block copolymers are disclosed in U.S. patent 4,959,436, which has been previously incorporated by reference for purposes of U.S. patent practice. With further modification

catalyst and co-catalyst were fed into a mixing tee as dilute solutions in hexane at a
temperature of 10°C. After mixing, the combined catalyst components flowed through
a tube with a residence time of 10 seconds at 10°C before entering the reactor. The
monomer feed to the reactor inlet was a solution of ethylene in hexane at 20°C which
5 was mixed with the catalyst stream to start the polymerization. The reactor was
operated adiabatically so that temperature increased along its length.

After a residence time of 0.024 minutes, during which the block A (polyethylene)
was formed, a feed of ethylene and propylene dissolved in hexane was added via a
10 sidestream injection point to begin polymerization of the B block. Two more ethylene-
propylene side feeds were added at residence times of 0.064 and 0.1 minutes to increase
the length of the B block. The polymerization was quenched with isopropanol at the end
of the reactor. The final reaction temperature was 22°C.

15 In Examples 1A and 1B no diene was used and the polymerization was quenched
at 0.14 min. The reaction conditions of polymerizations 1A and 1B are shown in Table
1.

Runs 1A and 1B

20

A number of polymerization experiments were carried out at the conditions used
in runs 1A and 1B, but with a polymerization quench injected into the reactor at a
residence time of 0.024 min. so that only polyethylene was produced. From the amount
of polymer collected in a known period of time, it was determined that close to 100% of
25 the ethylene fed to the reactor in the main flow had reacted to form polyethylene. Thus
in Examples 1A and 1B, the rate at which the polyethylene A block is produced is equal
to the feed rate of ethylene in the main flow. The rate at which the elastomeric B block
is produced can be found by subtracting the A block production rate from the measured
total polymerization rate. The percentages of A and B block in the polymer are then
30 calculated by dividing the respective polymerization rates of these blocks by the total
polymerization rate. The average ethylene content of the polymer is equal to the
ethylene content of the A block, which is 100%, times the fraction of the A block in the
polymer, plus the ethylene content of the B block times the fraction of B block in the
polymer. Thus the ethylene content of the B block can be calculated from the measured
35 average ethylene content of the whole polymer and the polymerization rates from the
equation:

- 26 -

Ethylene content of B block, weight percent = (average polymer %
ethylene content - 100 x weight fraction of A block in the total
polymer)/weight fraction of B block in the total polymer (all terms are in
5   weight units)

The ethylene content of the entire polymer was determined by infrared
spectroscopy using the calibration described in I. J. Gardner, C. Cozewith, and G.
Ver Strate, Rubber Chemistry and Technology, vol. 44, 1015, 1971.
10

The calculated polymer composition is shown in Table 2 along with other
measurements of the polymer structure (GPC and DSC). Of particular note is the
narrow MWD of the polymers.

Tensile properties of the polymers produced were determined in the following
15   manner. A sheet of polymer 15x15x0.2 cm was prepared by compression molding for 15
minutes at 150°C. An aluminum mold was used with Teflon® coated aluminum foil
used as a release agent. Dumbbell-type specimens were die cut from the sheet. These
specimens in turn were strained in tension at a crosshead speed of 12.5 cm/min. Initial
jaw separation was 5 cm. with 3.3 cm of the specimen undergoing most of the
20   deformation between the fiducial marks. Data were collected at 20°C. Engineering
modulii were calculated as force at a given percent elongation divided by the original
unstrained specimen cross-sectional area.

Table 3 shows the modulii and tensile strength of the polymer for runs 1A and 1B.
25   The mechanical properties are a function of molecular weight and the polyethylene block
content. The modulus of the polymer containing the larger amount of PE block (1A) are
slightly higher than that with a somewhat lower polyethylene block content (1B).

Example 2
30

A second series of polymerization runs were conducted following the procedures
outlined in Example 1. The initial monomer feed to the reactor contained only ethylene
to produce the polyethylene A block, two side stream feeds were then added to make the
B block. A final feed was introduced with a high ethylene content to produce a semi-
35   crystalline EP segment at the end or tip of the B block. Reaction conditions for runs 2A
and 2B are shown in Table 1. In example 2A, a higher initial ethylene feed rate was used

catalyst and co-catalyst were fed into a mixing tee as dilute solutions in hexane at a
temperature of 10°C. After mixing, the combined catalyst components flowed through
a tube with a residence time of 10 seconds at 10°C before entering the reactor. The
monomer feed to the reactor inlet was a solution of ethylene in hexane at 20°C which
was mixed with the catalyst stream to start the polymerization. The reactor was
operated adiabatically so that temperature increased along its length.

After a residence time of 0.024 minutes, during which the block A (polyethylene)
was formed, a feed of ethylene and propylene dissolved in hexane was added via a
sidestream injection point to begin polymerization of the B block. Two more ethylene-
propylene side feeds were added at residence times of 0.064 and 0.1 minutes to increase
the length of the B block. The polymerization was quenched with isopropanol at the end
of the reactor. The final reaction temperature was 22°C.

In Examples 1A and 1B no diene was used and the polymerization was quenched
at 0.14 min. The reaction conditions of polymerizations 1A and 1B are shown in Table
1.

Runs 1A and 1B

A number of polymerization experiments were carried out at the conditions used
in runs 1A and 1B, but with a polymerization quench injected into the reactor at a
residence time of 0.024 min. so that only polyethylene was produced. From the amount
of polymer collected in a known period of time, it was determined that close to 100% of
the ethylene fed to the reactor in the main flow had reacted to form polyethylene. Thus
in Examples 1A and 1B, the rate at which the polyethylene A block is produced is equal
to the feed rate of ethylene in the main flow. The rate at which the elastomeric B block
is produced can be found by subtracting the A block production rate from the measured
total polymerization rate. The percentages of A and B block in the polymer are then
calculated by dividing the respective polymerization rates of these blocks by the total
polymerization rate. The average ethylene content of the polymer is equal to the
ethylene content of the A block, which is 100%, times the fraction of the A block in the
polymer, plus the ethylene content of the B block times the fraction of B block in the
polymer. Thus the ethylene content of the B block can be calculated from the measured
average ethylene content of the whole polymer and the polymerization rates from the
equation:

- 26 -

Ethylene content of B block, weight percent = (average polymer % ethylene content - 100 x weight fraction of A block in the total polymer)/weight fraction of B block in the total polymer (all terms are in weight units)

The ethylene content of the entire polymer was determined by infrared spectroscopy using the calibration described in I. J. Gardner, C. Cozewith, and G. Ver Strate, Rubber Chemistry and Technology, vol. 44, 1015, 1971.

The calculated polymer composition is shown in Table 2 along with other measurements of the polymer structure (GPC and DSC). Of particular note is the narrow MWD of the polymers.

Tensile properties of the polymers produced were determined in the following manner. A sheet of polymer 15x15x0.2 cm was prepared by compression molding for 15 minutes at 150°C. An aluminum mold was used with Teflon® coated aluminum foil used as a release agent. Dumbbell-type specimens were die cut from the sheet. These specimens in turn were strained in tension at a crosshead speed of 12.5 cm/min. Initial jaw separation was 5 cm. with 3.3 cm of the specimen undergoing most of the deformation between the fiducial marks. Data were collected at 20°C. Engineering modulii were calculated as force at a given percent elongation divided by the original unstrained specimen cross-sectional area.

Table 3 shows the modulii and tensile strength of the polymer for runs 1A and 1B. The mechanical properties are a function of molecular weight and the polyethylene block content. The modulus of the polymer containing the larger amount of PE block (1A) are slightly higher than that with a somewhat lower polyethylene block content (1B).

Example 2

A second series of polymerization runs were conducted following the procedures outlined in Example 1. The initial monomer feed to the reactor contained only ethylene to produce the polyethylene A block, two side stream feeds were then added to make the B block. A final feed was introduced with a high ethylene content to produce a semi-crystalline EP segment at the end or tip of the B block. Reaction conditions for runs 2A and 2B are shown in Table 1. In example 2A, a higher initial ethylene feed rate was used

- 27 -

than in Example 2B to give the polymer a higher molecular weight and a greater percentage of A block.

These polymers were characterized in a manner similar to the polymers produced in Example 1. The results of these analyses are listed in Table 2. The semicrystalline end segment of the B block of Example 2A averaged 72.2 weight percent ethylene, while the semicrystalline end segment of the B block of Example 2B averaged 70 weight percent ethylene. DSC analysis of the polymers, as shown in Figures 1 and 2, show that the polymers contain a semi-crystalline fraction melting at 42° C in addition to a polyethylene fraction which melts at 122 to 124° C. The modulii and tensile strength of the polymers for runs 2A and 2B are shown in Table 3.

Example 3

A polymerization was carried out by the procedure in Example 1 using the reaction conditions as shown in Table 4 (samples 3A and 3B). The diene, ENB, was added to the main reactor feed to produce a polymer containing ENB in the PE block. Ethylene and propylene feeds were added to the reactor at residence times of 0.024 and 0.066 min. ENB feed rates were 2.8 and 1.7 g/hr. and the corresponding polymers contained 0.333 and 0.14 weight percent ENB. These polymers when coupled are useful as lubricating oil viscosity modifiers.

Example 4

In this example, a number of A B block polymers made by the procedure in Example 1 but over a broad range of reaction conditions, are tested for solubility in hexane at 22°C. The purpose of this testing is to determine how much B block is unconnected to an A block. The composition and molecular weight of the polymers vary widely. Solubility is determined by pressing 2.0 g of the block polymer onto a 20 mesh screen and immersing the polymer and screen in 200 cc of n-hexane. Wide-mouthed bottles were used and were occasionally swirled over a period of 3 to 5 days. The screen is removed and dried to constant weight in a vacuum oven to determine the amount of insoluble polymer. The hexane supernatant liquid is evaporated to dryness and the residue is weighed to measure the amount of soluble polymer. The sum of the two fractions showed 100% of the starting polymer is accounted for.

– 28 –

A control sample of a high density polyethylene which was melt blended with EPDM in a Brabender mixing head at 180°C was also extracted in the same manner. These results are presented in Table 5. In the control blend, all 40% of the EPDM was extractable, showing that the rubber is soluble, even at high PE block content, if it is not attached to a PE block. An infrared analysis showed the soluble material to be over 98% EPDM. PE is not extracted. All of the block polymers of Table 5 show soluble rubber of less than 25%.

Example 5   (Prophetic Example)

In this example analyses for PE block content and yield of A B block polymer as a percentage of the total product is described. Three A B block copolymers with a diene containing segment in the A block, are produced by the procedure described in Example 1. Nearly 100% of the ethylene has reacted by the time that the first ethylene/propylene side stream feed is added to make the elastomeric B block. Thus, the weight percent of A block in a polymer can be estimated by dividing the ethylene feed rate in the main flow to the reactor inlet by the total polymerization rate. We can also estimate the amount of A block by dividing the heat of fusion measured by DSC over the melting range of 80 °C to 135° C, by the heat of fusion measured by DSC for a pure polyethylene A block of approximately the same molecular weight, as shown in Figure 3, made by adding only an ethylene feed to the reactor.   A value of 181 J/g. is used for the heat of fusion of polyethylene based on averaging the results from a number of samples.

The polymer samples are fractionated in a Kumagawa apparatus. In this apparatus an individual sample is sequentially extracted with a series of solvents of increasing boiling point. For each solvent continuous extraction is carried out until all soluble polymer is dissolved. The solvents used and their boiling points (bp) were: n-hexane (bp=69°C), cyclohexane (bp=81°C), n-heptane (bp= 98°C), and toluene (bp= 111°C). The polymer soluble in each solvent is recovered, weighed, and analyzed by DSC. By determining the amount of polymer soluble in each solvent and the amount and percentage of PE block in that soluble portion, the percentage of the portion that was non-crystalline EP block can be calculated.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the

preferred versions contained herein.

TABLE 1

EXAMPLE	1A	1B	2A	2B
MAIN FLOW g/h				
hexane	53803	53803	53803	53803
propylene	0	0	0	0
ethylene	151	124	151	73
ENB	0	0	0	0
VCl4	1.8	1.5	2.4	2.4
Al/V mol/mol	8	8	8	8
SIDE STREAM 1, g/h				
hexane	8910	8910	8910	8910
propylene	1228	1354	1125	1125
ethylene	110	148	122	122
SIDE STREAM 2, g/h				
hexane	6138	6138	5910	5910
propylene	358	509	413	413
ethylene	85	110	130	130
SIDE STREAM 3, g/hr				
hexane	6217	6217	7920	7920
propylene	347	405	510	510
ethylene	80	108	255	255
TEMPERATURE, °C				
feed	20	20	19	19
reactor outlet	22	22	25	24
RESIDENCE TIME, min.				
to side stream 1	0.024	0.024	0.024	0.024
to side stream 2	0.064	0.064	0.109	0.109
to side stream 3	0.10	0.10	0.147	0.147
to side stream 4				
Total	0.139	0.139	0.183	0.183
PROCESS RESULTS				
wt % $C_2^=$ in polymer	71.6	70.8	72.2	70.1
wt % ENB in polymer	0	0	0	0
Mooney (1+4, 150°C)	109	91.1	114	131
Mw x 10-3	189	246	222	209
Mn x 10-3	108	149	115	106
Mw/Mn	1.67	1.7	1.91	1.99
Poly Rate, g/h	387	368	689	597
C2=conv *, %	65	54.8	75.6	72.2
C3=conv *, %	5.7	4.4	9.4	8.7
Cat eff,g poly/g VCl4	215	245.3	297	249

* conv = conversion

TABLE 2

Example	1A	1B	2A	2B
Poly rate A block, g/hr	151	124	151	73
Poly rate B block, g/hr	236	244	319	355
Poly rate C block, g/hr	0	0	259	265
A block, wt %	39.0	33.7	20.7	10.5
B block, wt %	61.0	66.3	43.7	51.2
C block, wt %	0	0	35.5	38.2
wt % C2= in whole polymer	71.6	72.9	72.2	70.1
wt % C2= in B block before final feed	53.4	59.1	59.0	63.9
wt % C2= in B block after final feed			72.2	70.1
wt % ENB whole polymer				
wt % ENB in EPDM segment				
GPC				
Mw x 10-3	189	246	221	209
Mn x 10-3	108	149	115	106
Mw/Mn	1.67	1.7	1.91	1.99
DSC Heat of Fusion J/g Total Polymer				
A block, J/g	48	33	29.2	21.3
B block, J/g		0.82	3.59	4.14
Wt. % soluble in n-hexane			2.3	2.6

5

TABLE 3

EXAMPLE	1A	1B	2A	2B
100% MODULUS, MPa	2.4	2.3	2.7	2.2
TENSILE STRENGTH AT BREAK, MPA	3.5	9.7	15.4	5.4
EXTENSION AT BREAK, %	780	1220	1090	740

TABLE 4   (Example 3)

EXAMPLE	3A	3B
RUN	397D	397E
RUN CONDITIONS		
MAIN FLOW g/h		
hexane	53605	53526
propylene	0	0
ethylene	253	253
diene	2.8	1.71
catalyst	3.36	3.36
Al/V, mol/mol		7
SIDE STREAM 1, g/h		
hexane	6692	6692
propylene	1234	1234
ethylene	111	111
SIDE STREAM 2, g/h		
hexane	9900	9900
propylene	468	471
ethylene	112	112
SIDE STREAM 3, g/hr		
hexane		
propylene		
ethylene		
ENB		
TEMPERATURES		
Reactor feed, °C	20	20
Reactor outlet, °C	31	31
RESIDENCE TIME, min		
to side stream 1	0.024	0.024
to side stream 2	0.066	0.066
to side stream 3		
Total	0.142	0.142
PROCESS RESULTS		
Wt. % C2=in polymer	73.2	71.5
Wt. % ENB in polymer	0.33	0.14
Mooney (1 + 4, 150°C)	51	49.8
A Block, % of polymer		
Poly Rate, g/h	592.5	604
C2= conv, % *	90.8	90.6
C3= conv, % *	9.3	10.1
ENB conv, % *	69.8	49.5
Cat eff, g poly/g VCl$_4$	176.4	179.8

5

*conv = conversion

TABLE 5

Run	Wt. % C2= in Poly.	Mn x 10-3	Mw x 10-3	Hexane soluble, %
317a	68	75	139	12.1
317b	68	97	193	13.0
317c	71	118	228	4.9
317d	69	92	189	12.5
318a	63	69	118	22.1
318b	62	62	118	23.5
318c	64	88	208	16.6
318d	66	92	179	16.9
319a	66	108	160	13.2
319c	68	108	230	7.8
320a	71	108	206	4.1
320c	70	128	237	3.3
323a	72	137	289	2.9
323b	71	152	307	2.2
332a	68	149	258	11.3
333a	68	104	212	7.7
334a	69	126	195	4.9
334b	67	117	178	8.0
335a	66	94	143	10.1
335b	70	-	-	6.5
336a	69	-	-	15.2
336d	66	-	-	19.0
336e	69	74	147	3.7
338b	-	-	-	6.0
60% HDPE/ 40% EPDM	-	-	-	39.6
40% HDPE/ 60% EPDM	-	-	-	61.0

- 33 -

Claims:

1.   A block copolymer comprising an A block, and a B block, wherein

said A block consists essentially of an ethylene polymer, optionally containing an alpha-olefin, said alpha-olefin being present in said A block at less than 5 mole percent, wherein said A block further contains a non-conjugated diene, wherein said A block has a T_m of at least 110° C;

said B block including a first polymer segment contiguous to a junction of said A block and said B block, said first segment comprising ethylene and an alpha-olefin;

said B block having a tip segment, said tip segment being furthest from said junction, said tip segment being a polymer of ethylene, and an alpha-olefin, wherein said tip segment has an ethylene content of at least 60 mole percent based on the total moles of the monomers of said tip segment, and wherein said B block melts in the range of from 35 to 130° C; and .

wherein said block copolymer is formed in the presence of a vanadium catalyst system, said vanadium catalyst system having a vanadium compound and an organoaluminum compound

2.   A block copolymer comprising an A block and a B block wherein;

said A block consists essentially of an ethylene, non-conjugated diene polymer, wherein said non-conjugated is present in said block copolymer in the range of from 0.03 to 2 mole percent based on the total moles in said block copolymer, wherein said non-conjugated diene is selected from the group consisting of 5-ethylidene-2-norbornene, vinylnorbornene, tetrahydroindene, 5-methylene-2-norbornene, dicyclopentadiene, tetrahydroindene, methyltetra-hydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2,5-diene, 5-propenyl-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, vinyl norbornene, and norbornadiene;

said B block includes an ethylene alpha-olefin copolymer;

- 34 -

said B block having an intramolecular composition distribution such that at least two portions of the B block, each portion comprising at least 5 weight percent of the block, differ in composition by at least 5 weight percent ethylene; and

5   wherein said block copolymer is formed in the presence of a vanadium catalyst system,   said vanadium catalyst system having a vanadium compound and an organoaluminum   compound.

3.   A block copolymer comprising an A block and a B block wherein;

10

said A block consists essentially of an ethylene polymer;

said B block being an ethylene alpha-olefin copolymer; and

15   said B block having an intramolecular composition distribution such that at least two portions of the B block, each portion comprising at least 5 weight percent of the block, differ in composition by at least 5 weight percent ethylene; and

wherein said block copolymer is formed in the presence of a vanadium catalyst 20   system,   said vanadium catalyst system having a vanadium compound and an organoaluminum   compound.

4.   A block copolymer comprising an A block and a B block, said B block having 2 or more segments, wherein the A block is an ethylene polymer optionally containing an 25   alpha-olefin and a non-conjugated diene wherein said non-conjugated is present in said block copolymer in the range of from 0.03 to 2 mole percent based on the total moles in said block copolymer, said alpha-olefin if present in said A block is present at less than 5 mole percent, said B block having at least one ethylene, α-olefin copolymer segment, and said B block having a tip segment of ethylene and an α-olefin,

30

said tip segment being at the end of said B block, said tip segment being furthest of said segments from an A B junction;

said block copolymer having a n-hexane soluble portion, not exceeding 30 35   weight percent based on the total weight of the block copolymer;

- 35 -

wherein said block copolymer is made by a process utilizing a vanadium catalyst system, wherein said vanadium catalyst system includes a vanadium compound premixed with an organoaluminum compound, said premixing being for a sufficient time to produce an adequate quantity of active catalyst; wherein said vanadium compound is represented by one of the general formulas:

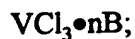$$\overset{O}{\overset{\|}{}}$$

$$VCl_x(OR)_{3-x}; \qquad\qquad (1)$$

$$VCl_x(COOR)_{3-x}; \qquad\qquad (2)$$

where x = 0 to 3 and R = a hydrocarbon radical;

$$VCl_4;$$

$$\overset{O}{\overset{\|}{}}$$

$$V(AcAc)_2;$$

where AcAc = acetyl acetonate;

$$V(AcAc)_3;$$

$$\overset{O}{\overset{\|}{}}$$

$$VCl_x(AcAc)_{3-x}; \qquad\qquad (3)$$

where x = 1 or 2; and

$$VCl_3 \bullet nB;$$

where n = 2 to 3 and B = Lewis base capable of making hydrocarbon-soluble complexes with VCl_3, where B is selected from the group consisting of tetrahydrofuran, 2-methyl-tetrahydrofuran and dimethyl pyridine, where R represents a C_1 to C_{10} aliphatic,

acylic, or aromatic hydrocarbon radical;

wherein the organoaluminum compound is represented by one of the formulas:

5   AlR_3, $Al(OR')R_2$
           AlR_2X $R_2Al-O-AlR_2$
           $AlR'RX$
           $Al_2R_3X_3$
           $AlRX_2$,
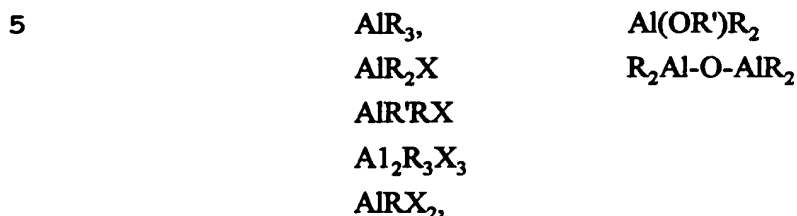
10

where R and R' represent hydrocarbon radicals, said R and R' being the same or different, wherein X is a halogen selected from the group consisting of bromine, chlorine, and iodine;

15   wherein said B block has an intra-molecular-composition distribution, wherein at least 2 portions of said B block each portion comprising at least 5 weight percent of said B block, said 2 portions differing in ethylene content by at least 5 weight percent;

wherein said alpha-olefin in said B block and said A block is propylene;

20

wherein said block copolymer is present at greater than 50 weight percent based on the total weight of polymer, as polymerized;

wherein said A B block copolymer has a Mw/Mn of less than 2.5; and

25

wherein said A block is present in said block copolymer in the range of from 10 to 60 weight percent.

5.   The block copolymer of any of claims 1-3 wherein said vanadium compound is
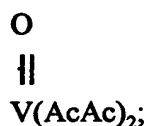30   represented by one of the general formulas:

$$\overset{\displaystyle O}{\underset{\displaystyle \|}{}} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (1)$$

VCl$_x$(OR)$_{3-x}$;

VCl$_x$(COOR)$_{3-x}$;   (2)

where x = O to 3 and R = a hydrocarbon radical;

VCl$_4$;

$$\overset{\displaystyle O}{\underset{\displaystyle \|}{}}$$

V(AcAc)$_2$;

where AcAc = acetyl acetonate;

V(AcAc)$_3$;

$$\overset{\displaystyle O}{\underset{\displaystyle \|}{}}$$

VCl$_x$(AcAc)$_{3-x}$;   (3)

where x = 1 or 2; and

VCl$_3$•nB;
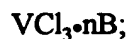
where n = 2 to 3 and B = Lewis base capable of making hydrocarbon-soluble complexes with VCl$_3$, wherein said B is selected from the group consisting of tetrahydrofuran, 2-methyl-tetrahydrofuran and dimethyl pyridine, where R represents a C$_1$ to C$_{10}$ aliphatic, acylic, or aromatic hydrocarbon radical;

wherein the organoaluminum compound is represented by one of the formulas:

- 38 -

$$AlR_3 \qquad\qquad Al(OR')R_2$$
$$AlR_2X \qquad\qquad R_2Al\text{-}O\text{-}AlR_2$$
$$AlR'RX$$
$$Al_2R_3X_3$$
$$AlRX_2$$
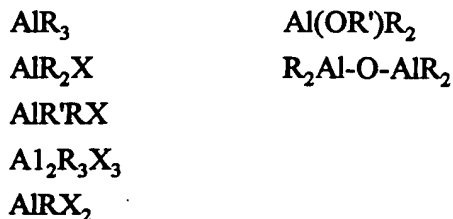
where R and R' represent hydrocarbon radicals, said R and R' being the same or different and wherein X is a halogen selected from the group consisting of bromine, chlorine, and iodine.

6.   The block copolymer of any of claims 1-4 wherein said block copolymer is present at greater than 50 weight percent based on the total weight of polymer as polymerized.

7.   The block copolymer of claims 1 or 2 wherein said B block has an intra-molecular-compositional distribution, wherein at least 2 portions of said B block each portion comprising at least 5 weight percent of said B block, said 2 portions differ in ethylene content by at least 5 weight percent.

8.   The block copolymer of claims 1-4, wherein said B block has an average ethylene content in the range of from 20 to 90 mole percent based on the total moles of the monomers of the B block.

9.   The block copolymer of any of claims 1-4 wherein said alpha-olefin, if present in one or both of said A block and or said B block, is propylene.

10.   The block copolymer of any of claims 1-4 wherein said tip segment is present in said B block at a level up to 50 weight percent based on the total weight of said B block.

11.   The block copolymer of any of claims 1-4, wherein said block copolymer has a Mw/Mn of less than 2.5.

12.   The block copolymer of any of claims 1-4, wherein said A block comprises in the range of from 5 to 90 preferably 10 to 60 weight percent of said block copolymer.

- 39 -

13.   The block copolymer of any of the claims 1-4, wherein said block copolymer has a number average molecular weight in the range of from 750 to 20,000,000.

14.   An oil composition comprising the block copolymer of any of claims 1-4, said composition selected from the group consisting of fuel oil, heating oil, and lubricating oil.

15.   A lubricating oil including a viscosity modifier and or a dispersant, said viscosity modifier being one of the block copolymer of any of claims 1-4 or a functionalized deravative of the block copolymer of any of claims 1-4, said viscosity modifier being a functionalized derivative of the block copolymer of any of claims 1-4.

16.   A functionalization reaction product comprising the block copolymer of any of claims 1-4.

17.   A lubricating oil concentrate or lubricating oil comprising the block copolymer of any of claims 1-4.

18.   The use of the block copolymer of claims 1-4 as a constituent in the group consisting of a thermoplastic elastomer, a thermoplastic blend, an hot melt adhesive, a bitumen blend, and a roof sheeting compound.

19.   The block copolymer of any of claims 1-4, wherein said block copolymer is coupled with at least another of said block copolymers wherein said coupling takes place in the presence of a coupling agent, said coupling agent being selected from the group consisting of AlX_3, BX_3,SnX_4, SbX_5, AlR_yX_{3-y} where y is 0 to 1.5, R is a hydrocarbon radical , BX_4, TiX_4 and mixtures thereof, where X is selected from the group consisting of chlorine, bromine, and iodine; or

said coupling agent being a free radical coupling agent selected from the group consisting of dicumyl peroxide, d-tertiarybutylperoxide, t-butylperbenzoate, 1,1-di(t-butylperoxy)-3,3,5-trimethyl cyclohexane, azo-bisisobutylnitrite, azodicarboxylate, and mixtures thereof; and

wherein said coupling agent being a free radical coupling agent selected from the group consisting of sulfur dichloride, disulfenyl halides, borane, dithioalkanes, and mixtures
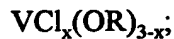
– 40 –

thereof; and

wherein said coupling agent being an alkyl phenol formaldehyde mixture catalyzed with a catalyst selected from the group consisting of $ZnCl_2$, N-bromosuccinimide and diphenylbromomethane;or

wherein said coupling agent being sulfur and a sulfur accelerator; and wherein said coupling takes place in a polymerization reactor or outside a polymerization reactor.

20.   The block copolymer of any of claims 1-4, wherein said A block contains in the range of from 0.05 to 1 mole percent of said non-conjugated diene based on the total moles of the monomers of the block copolymer.

21.   A process for preparing an olefin block copolymer, comprising the steps of:

(a)   forming a catalyst by premixing the reaction product of a vanadium compound represented by one of the formulas:
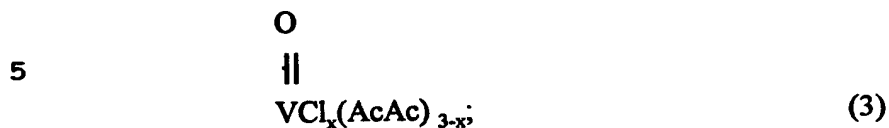
$$O$$
$$\overset{\|}{}$$ (1)

$$VCl_x(OR)_{3-x};$$

$$VCl_x(COOR)_{3-x};$$ (2)

where x = O to 3 and R = a hydrocarbon radical;

$$VCl_4;$$

$$O$$
$$\overset{\|}{}$$
$$V(AcAc)_2;$$

where AcAc = acetyl acetonate;

- 41 -

V(AcAc)$_3$;

$$VCl_x(AcAc)_{3-x};\qquad (3)$$

with the structure having an O double-bonded (shown as O over ‖ above VCl).

where x = 1 or 2; and

VCl$_3$•nB;

where n = 2 to 3 and B = Lewis base capable of making hydrocarbon-soluble complexes with VCl$_3$, where B is selected from the group consisting of tetrahydrofuran, 2-methyl-tetrahydrofuran and dimethyl pyridine, where R represents a C$_1$ to C$_{10}$ aliphatic, acylic, or aromatic hydrocarbon radical;

and an organoaluminum compound represented by one of the formulas:
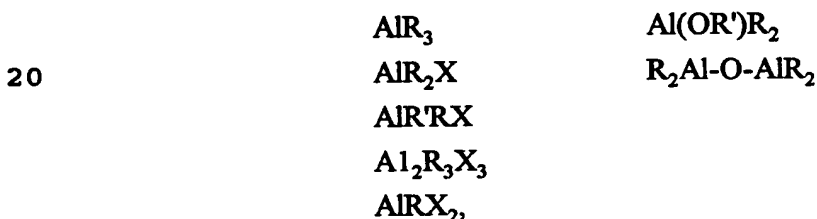
AlR$_3$ Al(OR')R$_2$
AlR$_2$X   R$_2$Al-O-AlR$_2$
AlR'RX
Al$_2$R$_3$X$_3$
AlRX$_2$,

where R and R' represent hydrocarbon radicals, said R and R' being the same or different, wherein X is a halogen selected from the group consisting of bromine, chlorine, and iodine;
said premixing being for a sufficient period of time to produce an adequate quantity of active catalyst;

(b)   feeding the reaction product of step (a) to a reactor concurrently with a monomer stream comprising ethylene, optionally an α-olefin, and optionally a non-conjugated diene; and then

(c)   feeding at least a second monomer blend comprising an ethylene and an α-olefin, at a time of at least 0.1 seconds after step (b).

- 42 -

22.   The process of claim 21, wherein said catalyst is comprised of VCl_4 as said vanadium compound and $Al_2R_3Cl_3$ as said organoaluminum compound, where R is an ethyl group.
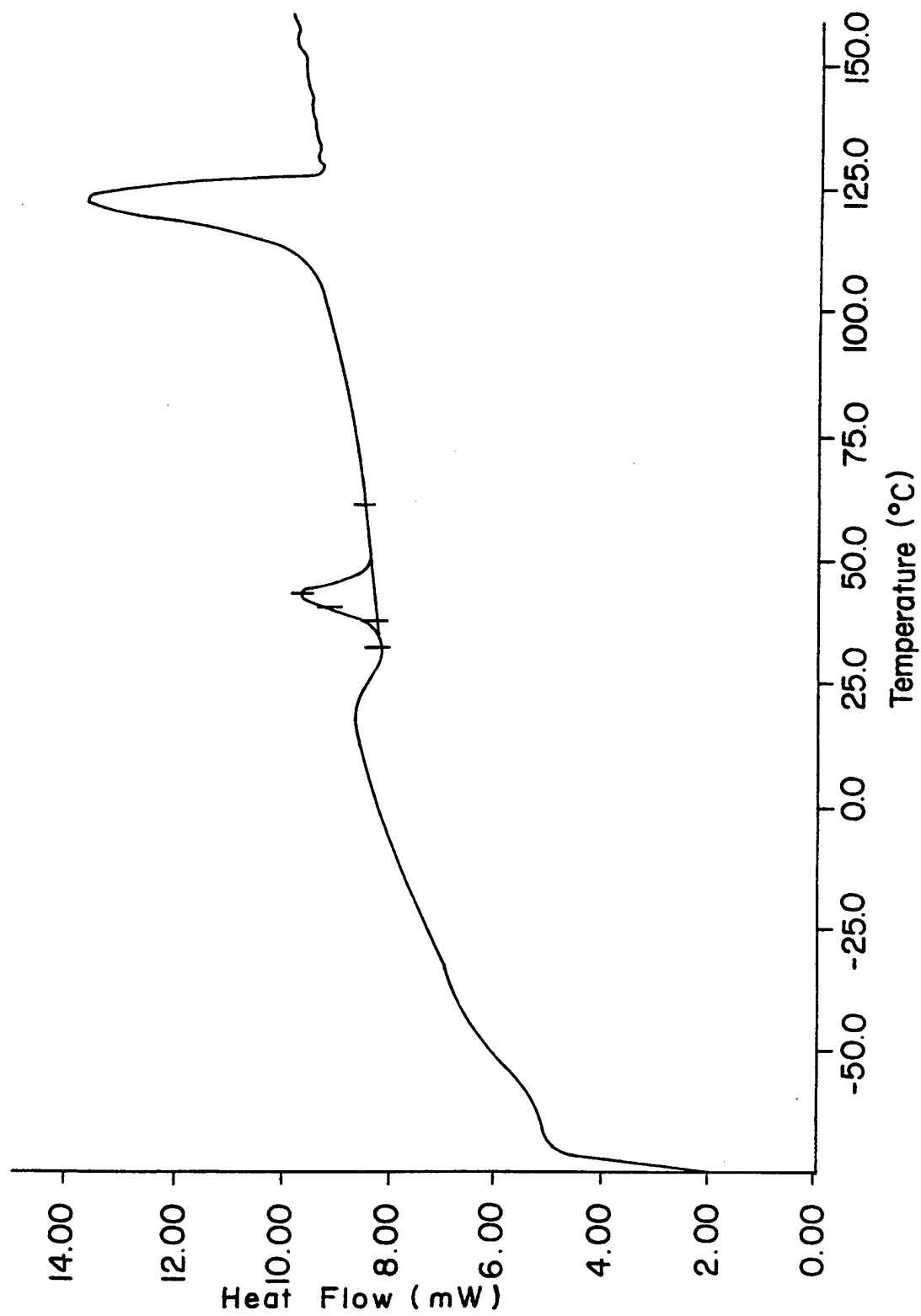
5

23.   The process of claim 21 wherein said non-conjugated diene, if present, is selected from the group consisting of 5-ethylidene-2-norbornene, vinylnorbornene, 5-methylene-2-norbornene, dicyclopentadiene, and tetrahydroindene.
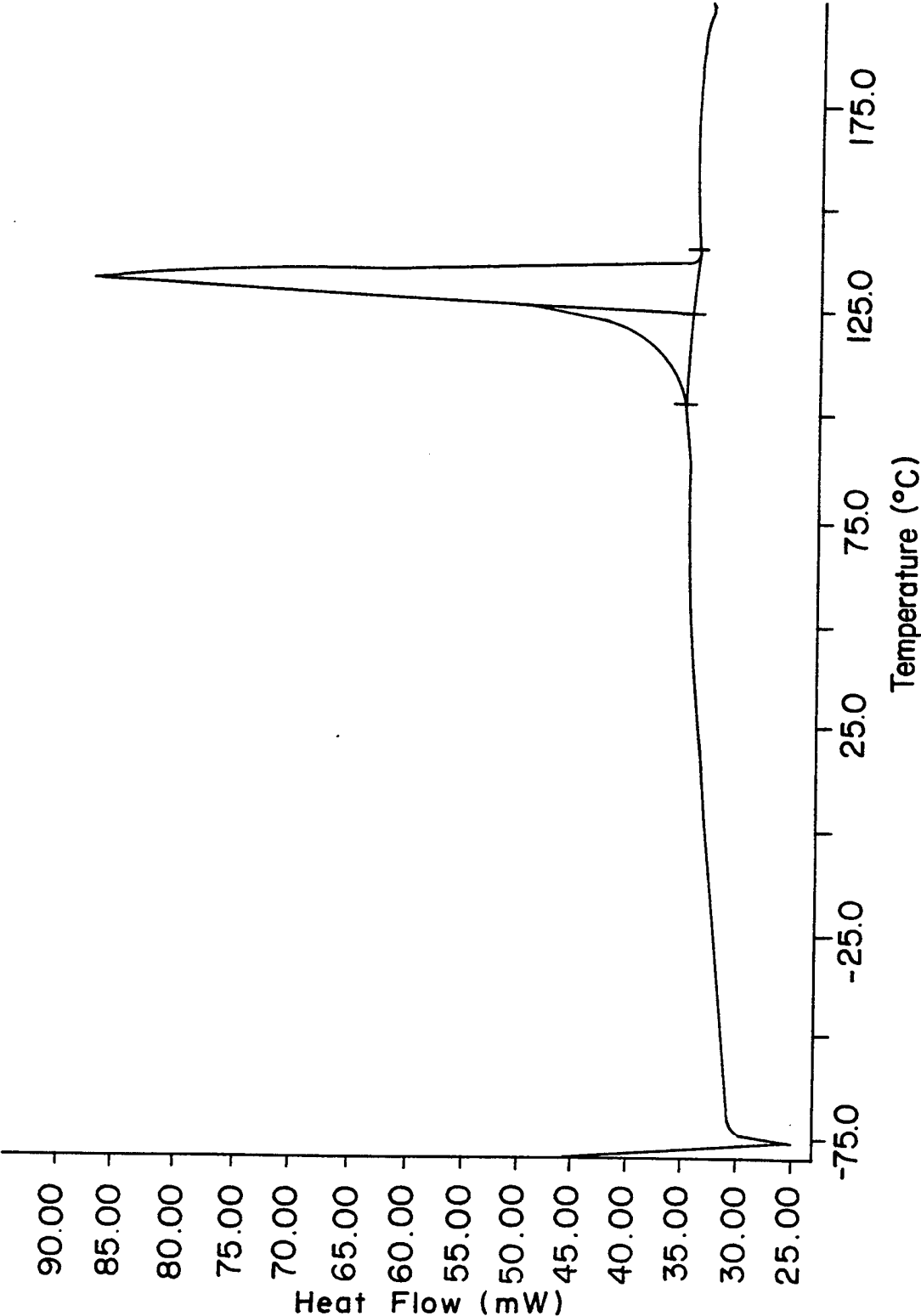
FIG.I
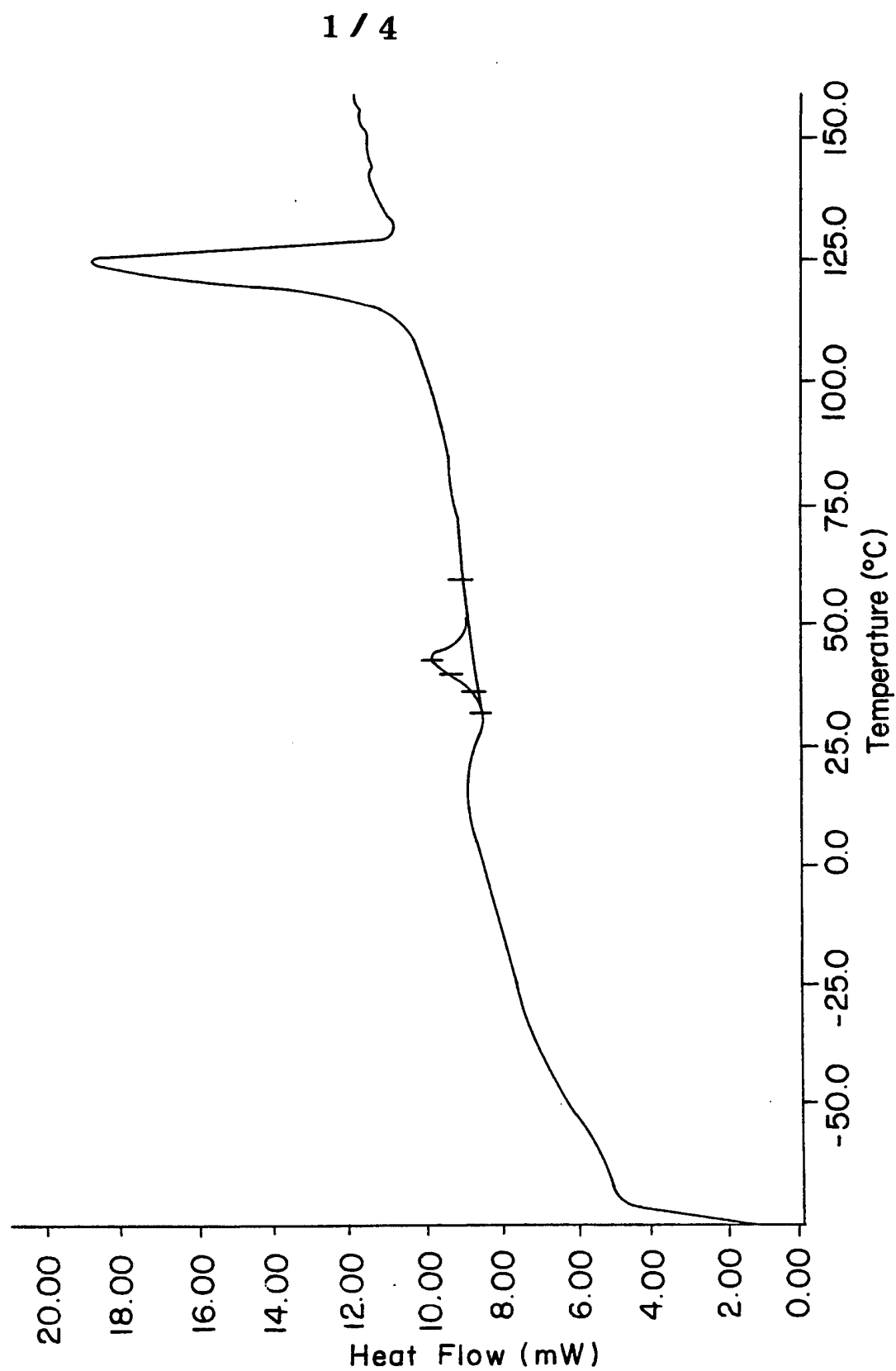
2 / 4

FIG.2

FIG.3

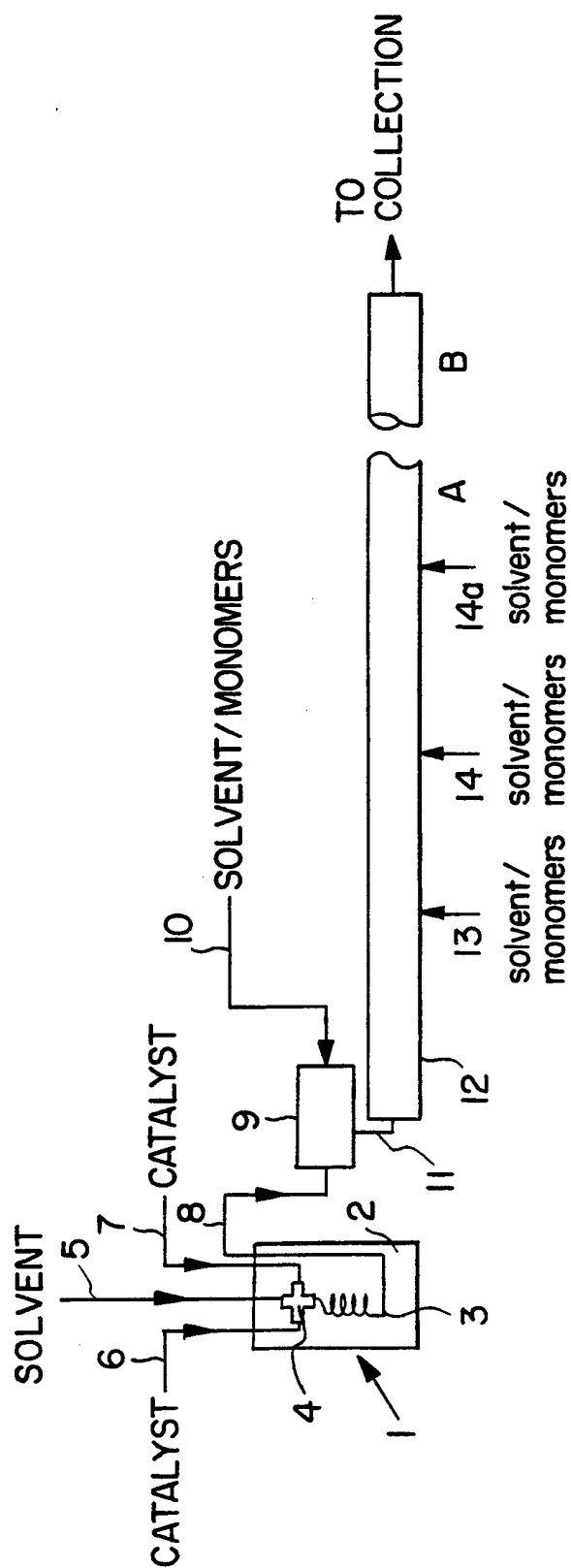4 / 4

FIG. 4

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C08F297/08   C10M143/02   C09J153/00   C08L53/00
//(C10M143/02,143:00),C10N20:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C08F   C10M   C09J   C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 175 670 (DUNLOP CO.) 23 December 1969 see claims; examples ---	1
Y	EP,A,0 129 414 (EXXON) 27 December 1984 cited in the application see page 22, line 16 - line 30; claims; examples 5A-B see page 21, line 18 - line 28 ---	1-23
Y	US,A,3 378 608 (HASSELL ET AL.) 16 April 1968 see claims; examples ---	1-23
Y	EP,A,0 299 608 (EXXON) 18 January 1989 cited in the application see claims 1,28,32,53; figure 1; tables IIIA-B --- -/--	1,14,15, 21-23

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 June 1995	12.06.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Loiselet-Taisne, S

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 798 288 (MCMANIMIE ET AL.) 19 March 1974 see claim 5 -----	1,14,15, 21-23

INTERNATIONAL SEARCH REPORT

...formation on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-1175670	23-12-69	NONE		
EP-A-129414	27-12-84	US-A-	4540753	10-09-85
		AU-B-	569304	28-01-88
		AU-A-	2938484	20-12-84
		AU-B-	608787	18-04-91
		AU-A-	8131687	10-03-88
		CA-A-	1228699	27-10-87
		JP-B-	6096624	30-11-94
		JP-A-	60035009	22-02-85
		JP-A-	6041239	15-02-94
		US-A-	4786697	22-11-88
		US-A-	4978720	18-12-90
		US-A-	4959436	25-09-90
		US-A-	5013801	07-05-91
		US-A-	5030695	09-07-91
		US-A-	4792595	20-12-88
		US-A-	4882406	21-11-89
		US-A-	4874820	17-10-89
		US-A-	4789714	06-12-88
		US-A-	4716207	29-12-87
US-A-3378608	16-04-68	NONE		
EP-A-299608	18-01-89	US-A-	4804794	14-02-89
		AU-B-	604319	13-12-90
		AU-A-	1643288	19-01-89
		CA-A-	1300775	12-05-92
		DE-A-	3882838	09-09-93
		DE-T-	3882838	11-11-93
		ES-T-	2058278	01-11-94
		JP-A-	1207309	21-08-89
		US-A-	4900461	13-02-90
US-A-3798288	19-03-74	NONE		